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 TI Austenitic steel weld joint with high resistance to weld cracking and sulfate corrosion and welding alloy for it
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AB The weld joint has a welded part having a composition containing C ≤ 0.08 , Mn ≤ 3 , P ≤ 0.02 , Ni 4-75, Cr 15-30, Al ≤ 0.5 , N ≤ 0.1 , O ≤ 0.1 , Nb, Ta, Ti, and/or Zr 0.1-5 in total, Mo and/or W 0-20 in total, Co 0-5, V 0-0.25, B 0-0.01, Ca 0-0.01, Mg 0-0.01, REM 0-0.01, Si $\leq [0.15(\text{Nb} + \text{Ta} + \text{Ti} + \text{Zr}) + 0.25]$, Cu 0-8 and $\leq [1.5(\text{Nb} + \text{Ta} + \text{Ti} + \text{Zr}) + 4.0]$, and S $\leq [0.0015(\text{Nb} + \text{Ta} + \text{Ti} + \text{Zr}) + 0.003]$ weight%, where (Ni + Co + 2Cu) is ≥ 25 weight%. The welding alloy is a Fe alloy containing C ≤ 0.08 , Si ≤ 2 , Mn ≤ 3 , P ≤ 0.02 , S ≤ 0.02 , Ni 4-75, Cr 15-30, Al ≤ 0.5 , N ≤ 0.1 , O ≤ 0.1 , Nb, Ta, Ti, and/or Zr 0.1-5 in total, Mo and/or W 0-20 in total, Co 0-5, Cu 0-8, V 0-0.25, B 0-0.01, Ca 0-0.01, Mg 0-0.01, and REM 0-0.01 weight%, where (Ni + Co + 2Cu) is ≥ 25 weight%. The weld joint is useful for high-temperature device such as boilers.

	≤ 0.08 C
	Si
	≤ 3 Mn
	≤ 0.02 P
	S
$0.1-5 \sum (\text{Nb, Ta, Ti, Zr})$	15-30 Cr
	4-75 Ni
$0-20 \sum (\text{Mo, W})$	0-8 Cu
	0.1-5 Nb
$0-0.01$ B	≤ 0.25 V
$0-0.01$ Mg	≤ 0.5 Al
$0-0.01$ REM	≤ 0.1 N
	≤ 0.1 O
	<hr/> Fe

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TI **Austenite** system steel welding joints has a welding metal having
a specified composition.
DC M27 P55
PA (SUMQ) SUMITOMO METAL IND LTD
CYC 1
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NOVELTY - An **austenite** system steel welding joint has welding metal containing specified amounts of carbon, manganese, phosphorus, nickel, chromium, aluminum, oxygen and nitrogen, at least one of niobium, tantalum, titanium and zirconium, at least one of molybdenum and tungsten, cobalt, vanadium, boron, calcium and magnesium, rare earth metal, silicon, copper, sulfur and iron.

DETAILED DESCRIPTION - An **austenite** system steel welding joint has welding metal containing (weight %): not greater than 0.08 of carbon (C), not greater than 3.0 of manganese (Mn), not greater than 0.02 of phosphorus (P), 4-75 of nickel (Ni), 15-30 of chromium (Cr), not greater than 0.5 of aluminum (Al), not greater than 0.1 of oxygen (O) and nitrogen (N), 0.1-5 of the total amount of at least one of niobium (Nb), tantalum (Ta), titanium (Ti), and zirconium (Zr), 0-20 of the total amount of at least one of molybdenum (Mo) and tungsten (W), 0-5 of cobalt (Co), 0-0.25 of vanadium (V), 0-0.01 of boron (B), 0-0.01 of (calcium, (Ca) and magnesium (Mg)), 0-0.01 of rare earth metal, silicon (Si) that satisfies relationship (1), copper (Cu) that satisfies relationship (2) and (4), sulfur (S) that satisfies relationship (3), and remainder is iron (Fe).

- Si at most $0.15(\text{Nb} + \text{Ta} + \text{Ti} + \text{Zr}) + 0.25$
(1)
Cu at most $1.5(\text{Nb} + \text{Ta} + \text{Ti} + \text{Zr}) + 4.0$
(2)
S at most $0.0015(\text{Nb} + \text{Ta} + \text{Ti} + \text{Zr}) + 0.003$ (3)
Ni + Co + 2Cu at least 25.
(4)

USE - None given.

ADVANTAGE - This welding joint can be welded in wide range of welding conditions and it has high toughness and also has high resistance against weld cracking and corrosion caused by sulfuric acid.
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(54) AUSTENITIC STEEL WELDED JOINT EXCELLENT IN WELD CRACKING RESISTANCE AND SULFURIC ACID CORROSION RESISTANCE AND THE WELDING MATERIAL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an austenitic steel welded joint excellent in weld cracking resistance and exhibiting good corrosion resistance in a sulfuric acid environment.

SOLUTION: The weld metal part of the joint is composed of a chemical composition containing $\leq 0.08\%$ C, $\leq 3\%$ Mn, $\leq 0.02\%$ P, 4 to 75% Ni, 15 to 30% Cr, $\leq 0.5\%$ Al, $\leq 0.1\%$ N, $\leq 0.1\%$ O, at least one or more kinds among Nb, Ta, Ti and Zr by 0.1 to 5% in total and 0 to 5% Co, furthermore containing Si satisfying the inequality of $Si \geq 0.15(Nb+Ta+Ti+Zr)+0.25$, Cu of 0 to 8% and also satisfying the inequality of $Cu \leq 1.5(Nb+Ta+Ti+Zr)+4.0$ and S satisfying the inequality of $S \leq 0.0015(Nb+Ta+Ti+Zr)+0.003$, and the balance substantially Fe, and in which the total content of Ni, Co and Cu satisfies the inequality of $Ni+Co+2Cu \geq 25$.

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CLAIMS

[Claim(s)]

[Claim 1] By mass %, C:0.08% or less, less than [Mn:3%], P:0.02% or less, nickel: 4-75%, Cr:15-30%, less than [aluminum:0.5%], N:0.1% or less, In total at least one or more sorts in Nb, Ta, Ti, and Zr O (oxygen):0.1% or less 0.1 - 5%, In total both Mo, or both [either or] 0 - 20%, Co:0-5%, V:0 - 0.25%, B:0 - 0.01%, calcium:0-0.01%, Mg:0-0.01%, and REM:0-0.01% are included, and it is (1) of further the following. At Si which fills a formula, and 0 - 8% And following (2) Cu which fills a formula, and following (3) S which fills a formula is contained. the remainder -- substantial -- from Fe -- becoming -- (4) of the following [content / of nickel, Co, and Cu / sum total] Austenitic steel welded joint excellent in the weld-cracking-proof nature characterized by having the weld metal section which consists of chemical composition with which a formula is filled, and a sulfuric-acid-proof corrosive.

$Si \leq 0.15(Nb+Ta+Ti+Zr)+0.25$ nickel+Co+2Cu ≥ 25 [] (4) -- here, the symbol of element in the above-mentioned (1) - (4) type means the content (mass %) of each element in a weld metal.... (1) Cu $\leq 1.5(Nb+Ta+Ti+Zr)+4.0$ (2) S $\leq 0.0015(Nb+Ta+Ti+Zr)+0.003$.. (3)

[Claim 2] A base material by mass % C:0.08% or less, less than [Si:1%], less than [:Mn:2%], P:0.05% or less, S:0.01% or less, nickel:10-30%, Cr:10-30%, Cu: 2-10%, Mo:1-6%, less than [aluminum:0.5%], N:0.1% or less, O (oxygen):0.1% or less, V:0 - 0.25%, B:0 - 0.01%, calcium: The austenitic steel welded joint excellent in the weld-cracking-proof nature according to claim 1 characterized by being austenitic steel with which the remainder consists of Fe substantially including 0-0.01%, Mg:0-0.01%, and REM:0-0.01%, and a sulfuric-acid-proof corrosive.

[Claim 3] By mass %, C:0.08% or less, less than [Si:2%], less than [:Mn:3%], P:0.02% or less, S:0.02% or less, nickel:4-75%, Cr:15-30%, aluminum: Less than [0.5%], N:0.1% or less, O (oxygen):0.1% or less, In total at least one or more sorts in Nb, Ta, Ti, and Zr 0.1 - 5%, In total both Mo, or both [either or] 0 - 20%, Co:0-5%, Cu: 0-8%, V:0 - 0.25%, B:0 - 0.01%, calcium:0-0.01%, Mg:0-0.01% and REM:0-0.01% -- containing -- the remainder -- substantial -- from Fe -- becoming -- (4) of the following [content / of nickel, Co, and Cu / sum total] Welding materials characterized by consisting of chemical composition with which a formula is filled.

nickel+Co+2Cu ≥ 25 (4) Here, it is (4). The symbol of element in a formula means the content (mass %) of each element in welding materials.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention is used for obtaining the austenitic steel welded joint excellent in the corrosion resistance which is used for elevated-temperature equipments, such as a boiler, and is especially used in a sulfuric-acid environment, and this welded joint, and relates to suitable welding materials.

[0002]

[Description of the Prior Art] Sulfur is contained in petroleum and coal which are used as fuels, such as an object for thermal power stations, and an industrial boiler. For this reason, at the time of combustion, a sulfur oxide is generated in exhaust gas. If exhaust gas temperature falls, this sulfur oxide will react with the moisture in gas, will serve as a sulfuric acid, will dew on the member front face below dew point temperature, and will produce the so-called sulfuric acid dew point corrosion.

[0003] Since the above phenomena arise, by the heat exchanger used for an exhaust gas system, the measures of holding exhaust gas temperature to an elevated temperature have been taken so that dew condensation may not arise conventionally.

[0004] However, from increase and the viewpoint of a deployment of energy need in recent years, in order to collect heat energy as effectively as possible, there is an inclination for exhaust gas temperature to become low, and in connection with this, the ingredient which has corrosion resistance to a sulfuric acid has come to be developed.

[0005] Especially, in recent years, the austenitic steel which secured corrosion resistance is proposed by adding Cu of 1 - 5 mass %, for example so that JP,4-346638,A, JP,6-128699,A, etc. may see.

[0006] When using the austenitic steel containing the above Cu(s) as the structure, it is possible to use a base material as welding materials as it is, to use the welding materials containing Cu of 2 as shown in JP,6-142980,A - 5 mass %, etc.

[0007] However, a base material receives adjustment of an organization by rolling and heat treatment after an ingot, and strong reservation is achieved. On the other hand, since a weld metal is used in the organization of a coagulation as in almost all cases, it is not easy for the segregation of an element to arise and to make corrosion resistance and reinforcement into a base material and an EQC in essence.

[0008] Therefore, when the welding materials of the same chemical composition as a base material are used, generally the corrosion resistance of a weld metal and reinforcement are inferior compared with a base material, and the welded joint equipped with the desired engine performance is hard to be obtained. Moreover, although the reinforcement in an elevated temperature was secured when the welding materials containing Cu shown in above-mentioned JP,6-142980,A were used, there was a problem that welded joints with the enough corrosion resistance in a sulfuric-acid environment were not obtained. Furthermore, the austenitic steel containing Cu shown in above-mentioned JP,4-346638,A and above-mentioned JP,6-128699,A had high weld-cracking susceptibility, and when it carried out multilayer peak welding in addition to a coagulation crack, the very very small crack occurred in the weld metal, and it had the problem that a healthy welded joint was not obtained.

[0009]

[Problem(s) to be Solved by the Invention] The purpose of this invention is not to have a very small crack in that interior, but use for obtaining the austenitic steel welded joint excellent in the weld-cracking-proof nature which moreover shows good corrosion resistance under a sulfuric-acid environment, and a sulfuric-acid-proof corrosive, and this welded joint, and offer suitable welding materials as well as a coagulation crack, even if a weld metal is a weld metal by which multilayer peak welding was carried out.

[0010]

[Means for Solving the Problem] The summary of this invention is in the austenitic steel welded joint excellent in the weld-cracking-proof nature of following (1), and a sulfuric-acid-proof corrosive, and the welding materials of following (2).

[0011] By mass %, (1) C:0.08% or less, less than [Mn:3%], P:0.02% or less, nickel: 4-75%, Cr:15-30%, less than [aluminum:0.5%], N:0.1% or less, In total at least one or more sorts in Nb, Ta, Ti, and Zr O (oxygen):0.1% or less 0.1 - 5%, In total both Mo, or both [either or] 0 - 20%, Co:0-5%, V:0 - 0.25%, B:0 - 0.01%, calcium:0-0.01%, Mg:0-0.01%, and REM:0-0.01% are included, and it is (1) of further the following. At Si which fills a formula, and 0 - 8% And Cu which fills the following (2) types and following (3) S which fills a formula is contained. the remainder -- substantial -- from Fe -- becoming -- (4) of the following [content / of nickel, Co, and Cu / sum total] Austenitic steel welded joint excellent in the weld-cracking-proof nature which has the weld metal section which consists of chemical composition with which a formula is filled, and a sulfuric-acid-proof corrosive.

[0012]

$Si \leq 0.15(Nb+Ta+Ti+Zr)+0.25 \text{ nickel}+Co+2Cu \geq 25$ [] (4) -- here, the symbol of element in the above-mentioned (1) - (4) type means the content (mass %) of each element in a weld metal.... (1) $Cu \leq 1.5(Nb+Ta+Ti+Zr)+4.0$ (2) $S \leq 0.0015(Nb+Ta+Ti+Zr)+0.003$.. (3)

[0013] By mass %, (2) C:0.08% or less, less than [Si:2%], less than [:Mn:3%], P:0.02% or less, S:0.02% or less, nickel:4-75%, Cr:15-30%, aluminum: Less than [0.5%], N:0.1% or less, O (oxygen):0.1% or less, In total at least one or more sorts in Nb, Ta, Ti, and Zr 0.1 - 5%, In total both Mo, or both [either or] 0 - 20%, Co:0-5%, Cu: 0-8%, V:0 - 0.25%, B:0 - 0.01%, calcium:0-0.01%, Mg:0-0.01% and REM:0-0.01% -- containing -- the remainder -- substantial -- from Fe -- becoming -- (4) of the following [content / of nickel, Co, and Cu / sum total] Welding materials which consist of chemical composition with which a formula is filled.

[0014]

$nickel+Co+2Cu \geq 25$ (4) Here, it is (4). The symbol of element in a formula means the content (mass %) of each element in welding materials.

[0015] As for the austenitic steel welded joint of this invention of the above (1), it is desirable that the base material is austenitic steel which has the chemical composition shown below. The austenitic steel is mass %. Namely, C:0.08% or less, Si: Less than [1%], less than [:Mn:2%], P:0.05% or less, S:0.01% or less, nickel: 10-30%, Cr:10-30%, Cu:2-10%, Mo:1-6%, aluminum: It is austenitic steel with which the remainder consists of Fe substantially including less than [0.5%], N:0.1% or less, O (oxygen):0.1% or less, V:0 - 0.25%, B:0 - 0.01%, calcium:0-0.01%, Mg:0-0.01%, and REM:0-0.01%.

[0016] Above-mentioned this invention was completed based on the knowledge expressed below.

[0017] When multilayer peak welding of the base material which consists of austenitic steel containing Cu is carried out using the welding materials which have the same chemical composition as a base material, it is as having mentioned above that a detailed crack occurs in a weld metal.

[0018] And it has generated in the grain boundary and the above-mentioned detailed crack is classified into the following two. That is, one of them is the stress-relief cracking of the grain boundary part into which Si and C have condensed notably, and other one is the stress-relief cracking of the grain boundary part into which S and Cu have condensed notably.

[0019] The former crack is to accept melting marks in the fracture surface, and for Si and C which were segregated to the grain boundary to combine with Fe of a matrix by the heat cycle of degree pass, to form a low melting point product, and for this to fuse. Moreover, the fracture surface is a grain boundary and the latter crack is for the fixing force of a grain boundary to decline by the segregation of S and Cu.

[0020] As an indispensable component, the two above-mentioned kinds of crack generating can be prevented, if one or more sorts in Nb, Ta, Ti, and Zr are added.

[0021] That is, each of Nb, Ta, Ti, and Zr has a very strong affinity with C, and fixes C as a MC (M is Nb, Ta, Ti, and Zr). Moreover, these elements generate the oxide (for example, Nb (S, O)) containing S, fix S, and also make a grain boundary crystallize lamellae-like carbide during coagulation, and complicate the configuration of the grain boundary.

[0022] In order that the amount of formation of the aforementioned low melting point product may decrease sharply, it stops generating the former crack, and in order that S and Cu may carry out distributed segregation in the complicated grain boundary in addition to the oxide containing S preventing the fixing force fall of the grain

boundary, it stops consequently, generating the latter crack.

[0023] However, while the above-mentioned effectiveness made one or more sorts in Nb, Ta, Ti, and Zr contain 0.1 to 5% in total, when the sum total content was made into A %, it carried out the knowledge of obtaining Si content only within the case where made Cu content below into % $(1.5 \times A + 4.0)$ below % $(0.15 \times A + 0.25)$, and S content is made below into % $(0.0015 \times A + 0.003)$.

[0024] Moreover, since it is easy to produce solidifying segregation etc. and a weld metal is used in the organization of a coagulation as as mentioned above, compared with a base material, corrosion resistance is inferior in it. However, when the sum total content (nickel+Co+2Cu) of nickel, Co, and Cu was 25% or more, the knowledge of reservation [the corrosion resistance under a high-concentration sulfuric-acid environment which the concentration of a sulfuric acid calls 70%, i.e., sulfuric-acid-proof corrosive,] being possible was carried out.

[0025]

[Embodiment of the Invention] Hereafter, the austenitic steel welded joint and welding materials of this invention are explained to a detail. In addition, "mass %" is meant "%" below.

[0026] First, the reason for having defined the chemical composition of a weld metal as mentioned above is explained.

[0027] C: 0.08% or less C is an element which makes stability the austenite phase which is a matrix. However, if it adds superfluously, while a weld thermal cycle will generate Cr carbon nitride and causing corrosion resistance degradation, it becomes the cause of a fall on the strength. Furthermore, C reacts with Fe in Si segregated to the grain boundary, and a matrix, generates a low melting point compound, and increases reheat crack sensitivity. For this reason, C content is made into 0.08% or less. A desirable upper limit is 0.05%. In addition, although the lower possible one of C content is desirable, since reduction of the degree of pole causes a cost rise, about 0.005% is sufficient as the minimum.

[0028] Si: Although added as a deoxidizer, segregate below $\{0.15 \times (\text{Nb} + \text{Ta} + \text{Ti} + \text{Zr}) + 0.25\}$ % Si to the grain boundary at the time of the coagulation of a weld metal, and it reacts with Fe of C and a matrix, generates a low melting point compound, and causes stress-relief cracking at the time of multilayer welding. If this reheat crack sensitivity adds one or more sorts in Nb, Ta, Ti, and Zr which are mentioned later and fixes C, it will fall, but if Si content exceeds $\{0.15 \times (\text{Nb} + \text{Ta} + \text{Ti} + \text{Zr}) + 0.25\}$ %, sufficient stress-relief cracking-proof nature will not be secured. For this reason, Si content is made below into $\{0.15 \times (\text{Nb} + \text{Ta} + \text{Ti} + \text{Zr}) + 0.25\}$ %. In addition, as Si content is low, when the deoxidation effectiveness needs to be acquired, it is better [when sufficient aluminum, sufficient Mn, etc. for deoxidation are included, it is not necessary to necessarily add but, and / it is good, and] to make it contain about 0.02% or more.

[0029] Mn: Mn is added as a deoxidizer 3% or less, and make stability the austenite phase which is a matrix. However, if it adds to an excess not much, while using [an elevated temperature and] long duration, generation of an intermetallic compound will be promoted, and embrittlement will be caused. For this reason, Mn content is made into 3% or less. A desirable upper limit is 2%. In addition, especially a minimum does not need to set. Moreover, when deoxidation is fully performed by other elements (Si, aluminum), additive-free is sufficient as Mn.

[0030] P: 0.02% or less P is an unescapable impurity, in the case of welding, it is segregated in the last coagulation section at the time of the coagulation of a weld metal, reduces the melting point of a residual liquid phase, and generates a coagulation crack. For this reason, P content is made into 0.02% or less. A desirable upper limit is 0.015%. In addition, as long as there is no problem in a manufacturing cost, as P content is low, it is better.

[0031] S: Below $\{0.0015 \times (\text{Nb} + \text{Ta} + \text{Ti} + \text{Zr}) + 0.003\}$ is the same unescapable impurity as the above-mentioned P, and segregate it to the grain boundary, it reduces the fixing force of a grain boundary, and causes stress-relief cracking generating while forming the eutectic object of the low melting point at the time of the coagulation of a weld metal and generating a coagulation crack in the case of welding. [S] If this reheat crack sensitivity makes the oxide which adds one or more sorts in Nb, Ta, Ti, and Zr which are mentioned later like the case of the above-mentioned Si, and contains S form and S is fixed, it will fall, but if S content exceeds $\{0.0015 \times (\text{Nb} + \text{Ta} + \text{Ti} + \text{Zr}) + 0.003\}$ %, sufficient stress-relief cracking-proof nature will not be secured. For this reason, S content is made below into $\{0.0015 \times (\text{Nb} + \text{Ta} + \text{Ti} + \text{Zr}) + 0.003\}$ %. In addition, as long as there is no problem in a manufacturing cost, as S content is low, it is better.

[0032] nickel: In order to secure the corrosion resistance in the inside of the environment containing a high-

concentration sulfuric acid, 4 - 75%nickel is an indispensable element while stabilizing the austenite phase which is a matrix. In order to secure sufficient corrosion resistance, 25% or more is required of the sum total content of the amount of Co(es) and the twice as many amount of Cu(s) as this effective in raising the corrosion resistance in a sulfuric-acid environment like nickel which are mentioned later. However, while superfluous addition raises weld-cracking susceptibility, since nickel is an expensive element, it causes a cost rise. For this reason, nickel content is made into 4 - 75%.

[0033] Cr: 15-30%Cr is an effective element for reservation of oxidation-resistant [in an elevated temperature], and corrosion resistance, and in order to secure the corrosion resistance in the inside of the environment containing a high-concentration sulfuric acid, it is an indispensable element. In order to secure sufficient oxidation resistance and corrosion resistance, 15% or more is required. However, superfluous addition degrades workability remarkably while degrading corrosion resistance on the contrary. For this reason, Cr content is made into 15 - 30%. In addition, a desirable upper limit is 25%.

[0034] Form the oxide which is [in Nb, Ta, Ti, and more than Zr:1 sort] the most important element in this invention 0.1 to 5% in total, and fixes C in a weld metal as carbide, and contains S, and the fixing force of the grain boundary is raised, and also carbide is crystallized, the configuration of the grain boundary is complicated, these elements distribute the grain boundary segregation of S and Cu, and the stress-relief cracking at the time of multilayer peak welding is prevented. In order to acquire the effectiveness, it is necessary to make one or more sorts in Nb, Ta, Ti, and Zr contain 0.1% in total also at the lowest. However, the superfluous addition which exceeds 5% in total degrades workability while it causes big and rough-ization of carbide and causes degradation of toughness. For this reason, the content of these elements makes one or more sorts 0.1 - 5% in total. In addition, a desirable upper limit is 4.5.

[0035] aluminum: Although aluminum is added as a deoxidizer 0.5% or less, if contained so much, during welding, a slag will be generated, the fluidity of a weld metal and the homogeneity of a weld bead will be degraded, and welding workability will be reduced remarkably. Moreover, the welding condition field which carries out back wave formation is narrowed. For this reason, it is necessary to make aluminum content into 0.5% or less. A desirable upper limit is 0.3% and a more desirable upper limit is 0.2%.

[0036] Although N:0.1%or less N is an element effective in reservation on the strength, if contained so much, during an elevated temperature and use of long duration, it will deposit a lot of nitrides and will cause embrittlement. For this reason, N content is made into 0.1% or less. A desirable upper limit is 0.08% and a more desirable upper limit is 0.06%.

[0037] O (oxygen):0.1%or less O is an unescapable impurity, and if contained so much, cleanliness will deteriorate remarkably and it will cause embrittlement. For this reason, O content is made into 0.1% or less. A desirable upper limit is 0.08% and a more desirable upper limit is 0.06%.

[0038] Cu: Although it is less than [8%], and it is an element effective in raising the corrosion resistance in a high-concentration sulfuric-acid environment if it adds although it is not necessary to add below $\{1.5x(Nb+Ta+Ti+Zr) + 4.0\}$ % Cu and the effectiveness becomes remarkable at 0.5% or more, if it is made to contain exceeding 8%, the melting point of the liquid phase which carries out the last coagulation will be reduced, and a coagulation crack will be generated. Moreover, at the time of coagulation, Cu is segregated to the grain boundary, reduces the fixing force of a grain boundary, and causes the stress-relief cracking at the time of multilayer welding. As described above, since the grain boundary segregation of Cu is distributed by the complication effectiveness of the grain boundary by one or more sorts of addition of Nb, Ta, Ti, and the Zr, this reheat crack sensitivity falls, but if Cu content exceeds $\{1.5x(Nb+Ta+Ti+Zr) + 4.0\}$ %, sufficient stress-relief cracking-proof nature will not be secured. For this reason, Cu content in the case of adding is 8% or less, and is good to carry out to below $\{1.5x(Nb+Ta+Ti+Zr) + 4.0\}$ %.

[0039] Although these elements do not need to add Mo and W:1 or more sorts 20% or less in total, if it adds, it will be an element effective in raising the corrosion resistance in a high-concentration sulfuric-acid environment, and the effectiveness will become remarkable at 1% or more of sum total contents of either or both. However, if the sum total content exceeds 20%, generation of the compound between carbide metallurgy groups will be caused [that the effectiveness is saturated and] on the contrary while in use, and it will become the cause of corrosion resistance and toughness degradation. For this reason, the content of these elements in the case of adding is good to consider as 20% or less in total.

[0040] Co: Although it is not necessary to add less than [5%] Co, if it adds, while stabilizing an austenite phase like the aforementioned nickel, it is an element effective in raising the corrosion resistance in a high-

concentration sulfuric-acid environment, and the effectiveness becomes remarkable at 0.5% or more. However, Co is a very expensive element compared with the aforementioned nickel, and abundant addition causes a cost rise. For this reason, Co content in the case of adding is good to consider as 5% or less. A desirable upper limit is 4.5% and a more desirable upper limit is 4%.

[0041] Although it is not necessary to add V:0.25% or less V, if it adds, it will be an element effective in raising high temperature strength, and the effectiveness will become remarkable at 0.05% or more. However, superfluous addition deposits a lot of carbon nitride, and causes the fall of toughness. For this reason, V content in the case of adding is good to consider as 0.25% or less.

[0042] Although it is not necessary to add B:0.01% or less B, if it adds, it will segregate to the grain boundary and the reinforcement of a grain boundary will be raised, it is the element which has the effectiveness of reducing reheat crack sensitivity, and the effectiveness becomes remarkable at 0.0005% or more. However, superfluous addition promotes the coagulation crack at the time of welding conversely. For this reason, B content in the case of adding is good to consider as 0.01% or less. A desirable upper limit is 0.009% and a more desirable upper limit is 0.008%.

[0043] calcium: Although it is not necessary to add calcium 0.01% or less, if it adds, an affinity with S is strong, a sulfide will be formed, S will be fixed, it will be the element which has the effectiveness which raises stress-relief cracking-proof nature, and the effectiveness will become remarkable at 0.0005% or more. However, superfluous addition makes inclusion increase and degrades cleanliness. For this reason, calcium content in the case of adding is good to consider as 0.01% or less. A desirable upper limit is 0.009% and a more desirable upper limit is 0.008%.

[0044] Mg: Although it is not necessary to add Mg 0.01% or less, if it adds, like the above-mentioned calcium, an affinity with S is strong, a sulfide will be formed, S will be fixed, it will be the element which has the effectiveness which raises stress-relief cracking-proof nature, and the effectiveness will become remarkable at 0.0005% or more. However, superfluous addition makes inclusion increase and degrades cleanliness. For this reason, Mg content in the case of adding is good to consider as 0.01% or less. A desirable upper limit is 0.009% and a more desirable upper limit is 0.008%.

[0045] REM: Although it is not necessary to add REM 0.01% or less, if it adds, an affinity with S is strong, the amount of S which generates a high-melting sulfide and is segregated to the grain boundary will be reduced, it will be the element which has the effectiveness of reducing reheat crack sensitivity, and the effectiveness will become remarkable at 0.0005% or more. However, it causes a toughness fall while superfluous addition makes inclusion increase, spoils cleanliness and degrades corrosion resistance on the contrary. For this reason, the REM content in the case of adding is good to consider as 0.01% or less. A desirable upper limit is 0.009% and a more desirable upper limit is 0.008%.

[0046] It is desirable to use the austenitic steel which has the following chemical composition for the austenitic steel of the base material which constitutes the austenitic steel welded joint of this invention equipped with the weld metal which has the above-mentioned chemical composition.

[0047] The austenitic steel is mass %. Namely, C:0.08% or less, Si: Less than [1%], less than [:Mn:2%], P:0.05% or less, S:0.01% or less, nickel: 10-30%, Cr:10-30%, Cu:2-10%, Mo:1-6%, aluminum: It is austenitic steel with which the remainder consists of Fe substantially including less than [0.5%], N:0.1% or less, O:0.1% or less, B:0 - 0.01%, calcium:0-0.01%, Mg:0-0.01%, and REM:0-0.01%, and the reason is as follows.

[0048] Since Cr carbon nitride generates C especially in a heat affected zone and it becomes impossible to secure desired corrosion resistance when the content exceeds 0.08%, it is desirable. [0.08% or less of]

[0049] Since Si content in a weld metal will increase and the reheat crack sensitivity of a weld metal will become high by dilution if the content exceeds 1%, 1% or less of Si is desirable.

[0050] Although Mn is added as a deoxidizer, if superfluous addition is carried out extremely, since an intermetallic compound will be generated while using an elevated temperature and embrittlement will be caused, 2% or less is desirable.

[0051] Since P content of P in a weld metal will increase and coagulation crack sensitivity will raise it by dilution if the content exceeds 0.05%, 0.05% or less is desirable.

[0052] Since S content in a weld metal will increase and the reheat crack sensitivity of a weld metal will become high by dilution if the content exceeds 0.01%, 0.01% or less of S is desirable.

[0053] Since nickel will cause increase of a manufacturing cost if an austenite phase becomes it unstable that the content is less than 10% and it exceeds 30% conversely, 10 - 30% is desirable.

- [0054] Since Cr will cause a deposit of a lot of carbide and will reduce toughness while workability deteriorates remarkably, and using [a heat affected zone or] an elevated temperature if corrosion resistance becomes inadequate that the content is less than 10% and it exceeds 30% conversely, it is desirable. [10 - 30% of]
- [0055] Since workability will deteriorate remarkably if the corrosion resistance under a high-concentration sulfuric-acid environment becomes non-** for the content to be less than 2% and it exceeds 10% conversely, 2 - 10% of Cu is desirable.
- [0056] Since Mo will cause generation of a lot of compounds between carbide metallurgy groups and will reduce toughness while using [a weld thermal cycle or] an elevated temperature if the corrosion resistance under a high-concentration sulfuric-acid environment becomes non-** for the content to be less than 1% and it exceeds 6% conversely, it is desirable. [1 - 6% of]
- [0057] As for aluminum, N, and O (oxygen), it is desirable that each is [aluminum] 0.1% or less about 0.5% or less, and N and O by the same reason as the case of a weld metal.
- [0058] Although B does not need to contain, since the content of B content in a weld metal increases depending on super-***** and dilution 0.01% and the coagulation crack sensitivity of a weld metal becomes high when it contains, as for B content in the case of containing, it is desirable that it is 0.01% or less.
- [0059] Although all calcium, Mg, and REM need to contain, when it contains, as for the content of these elements since 0.01% super-*****, and inclusion increase and spoil cleanliness, in case the content contains any element, it is desirable that any element is 0.01% or less.
- [0060] In addition, B, calcium, Mg, and REM in the case of containing raise hot-working nature. Moreover, about REM, when it dilutes in a weld metal, a high-melting sulfide is formed, S segregation to the grain boundary is controlled, and the stress-relief cracking nature susceptibility of a weld metal is reduced.
- [0061] Moreover, it uses in order to obtain the weld metal which has the above-mentioned chemical composition which constitutes the austenitic steel welded joint of this invention, and suitable welding materials are welding materials which have the following chemical composition.
- [0062] The welding materials are mass %. Namely, C:0.08% or less, less than [Si:2%], : Less than [Mn:3%], P:0.02% or less, S:0.02% or less, nickel:4-75%, Cr: 15-30%, less than [aluminum:0.5%], N:0.1% or less, O:0.1% or less, In total at least one or more sorts in Nb, Ta, Ti, and Zr 0.1 - 5%, In total both Mo, or both [either or] 0 - 20%, Co:0-5%, Cu: 0-8%, V:0 - 0.25%, B:0 - 0.01%, calcium:0-0.01%, Mg: It is ***** which the remainder consists of Fe substantially and consists of chemical composition with which the sum total content of nickel, Co, and Cu fills a formula "nickel+Co+2Cu>=25" including 0-0.01% and REM:0-0.01%, and the reason is as follows.
- [0063] In order to give sufficient engine performance for a weld metal, as for C content, it is desirable that it is 0.08% or less.
- [0064] Since Si will increase Si content in a weld metal and will increase reheat crack sensitivity while it degrades remarkably the hot-working nature at the time of welding-materials manufacture if the content exceeds 2%, it is desirable that it is 2% or less.
- [0065] Since Mn will cause generating of a lot of fume at the time of welding while degrading the hot-working nature at the time of welding-materials manufacture if the content exceeds 3%, it is desirable that it is 3% or less.
- [0066] As for P content, it is desirable that it is 0.02% or less by the same reason as the case of a weld metal.
- [0067] Since S will increase S content in a weld metal and will increase coagulation crack sensitivity and reheat crack sensitivity while it degrades the hot-working nature at the time of welding-materials manufacture if the content exceeds 0.02%, it is desirable that it is 2% or less.
- [0068] As for nickel content, it is desirable that it is the amount which is 4 - 75% and fills a formula "nickel+Co+2Cu>=25" for the same reason as the case of a weld metal.
- [0069] In order to give sufficient stress-relief cracking-proof nature for a weld metal, as for Cr content, it is desirable that it is 10 - 30%.
- [0070] Although Nb, Ta, Ti, and Zr make one or more sorts contain as an indispensable component, in order to give sufficient stress-relief cracking-proof nature for a weld metal, as for the content, it is desirable that it is 0.1 - 5% in total.
- [0071] As for each content of aluminum, N, and O (oxygen), it is desirable that each is [aluminum] 0.1% or less about 0.5% or less, and N and O by the same reason as the case of a weld metal.
- [0072] Although Cu does not need to contain, since the content reduces remarkably the hot-working nature at

the time of 8% super-*****, and welding-materials manufacture when it contains, as for the content in the case of containing, it is desirable that it is 8% or less.

[0073] Although Mo and W do not need to contain, in order to give the engine performance required for a weld metal, as for a content in case either or both are included, it is desirable that it is 20% or less in total.

[0074] Although Co does not need to contain, in order to give the engine performance required for a weld metal, as for the content in the case of containing, it is desirable that it is 5% or less.

[0075] Although V may not have *****, in order to give the engine performance required for a weld metal, as for the content in the case of containing, it is desirable that it is 0.25% or less.

[0076] Although B does not need to contain, in order to give the engine performance required for a weld metal, as for the content in the case of containing, it is desirable that it is 0.01% or less.

[0077] Although all calcium, Mg, and REM need to contain, in order to give the engine performance required for a weld metal, as for the content of each element in the case of containing, it is desirable that any element is 0.01% or less.

[0078] In addition, B, calcium, above-mentioned Mg, and above-mentioned REM in the case of containing raise hot-working nature. Moreover, about REM, a high-melting sulfide is formed, S segregation to the grain boundary is controlled, and the reheat crack sensitivity of a weld metal is reduced.

[0079] what has the chemical composition the weld metal prescribes the above-mentioned welded joint which becomes this invention by this invention -- it is even -- if it carries out -- TIG -- law and MIG -- even when there is no effect by welding processes, such as a gas-shielded-arc-welding method represented by law, a stick welding method, and a submerged-arc-welding method, and it manufactures with which welding process, sufficient weld-cracking-proof nature and a sulfuric-acid-proof corrosive are shown.

[0080] Moreover, there are no special conditions in the welding condition in the case of manufacturing the above-mentioned welded joint which becomes this invention with each above-mentioned welding process.

[0081]

[Example] The base material steel plate of 12mm of board thickness which has the chemical composition shown in Table 1 was prepared. The corrosion rates per unit area when this base material steel plate is immersed for 8 hours into the sulfuric-acid solution which is 100 degrees C of solution temperature whose sulfuric-acid concentration is 70% are below 2.0 g/m² and hr.

[0082]

[Table 1]

表 1							
化 学 組 成 (質量%)							
C	Si	Mn	P	S	Ni	Cu	Cr
0.02	0.50	0.96	0.020	0.005	15.12	4.62	17.96

Mo	Al	N	O	B	Ca
2.60	0.018	0.018	0.008	0.003	0.003

注) 残部は実質的にFeである。

[0083] Moreover, it has the chemical composition shown in Table 2 and Table 3, and the welding materials (welding wire) which are 12 kinds whose outer diameters are 1.2mm were prepared except No.A4. In addition, the welding materials of No.A4 are the covered electrodes which applied the cladding material which becomes the periphery of a welding wire with an outer diameter of 4mm from a metal carbonate, metal fluoride, Si compound, Ti compound, and metal powder.

[0084]

[Table 2]

表 2

No	化 学 組 成 (質量%)											
	C	Si	Mn	P	S	Ni	Cr	Cu	Nb	Ta	Ti	Zr
A1	0.04	0.28	1.20	0.017	0.004	70.32	18.13	0.01	1.56	0.33	—	—
A2	0.06	0.36	0.84	0.015	0.002	64.12	21.36	0.01	3.13	—	0.96	—
A3	0.05	0.15	0.96	0.020	0.002	54.21	17.35	0.01	0.12	—	—	0.08
A4	0.03	0.23	0.54	0.009	0.004	72.11	15.63	1.05	—	1.03	—	—
A5	0.05	0.15	1.08	0.011	0.001	49.16	21.33	0.03	0.18	—	—	—
A6	0.05	0.20	0.75	0.010	0.003	31.18	20.18	—	2.02	—	—	—
B1	0.04	0.16	1.56	0.018	0.003	43.16	18.71	2.21	—	—	—	0.08
B2	0.04	1.24	0.48	0.013	0.001	85.23	12.36	0.01	—	—	0.26	—
B3	0.02	0.21	0.96	0.014	0.016	70.02	17.36	4.67	—	0.56	0.08	0.12
B4	0.03	0.56	0.44	0.015	0.003	80.32	20.13	3.54	7.41	—	—	—
B5	0.03	0.33	1.03	0.018	0.003	55.13	18.12	10.16	2.08	—	—	0.81
B6	0.05	0.22	0.84	0.011	0.002	17.26	22.65	0.03	1.08	0.11	—	—

[0085]

[Table 3]

表 3 (表 2 の続き)

No	化 学 組 成 (質量%)										
	Al	N	O	Mo	W	Co	Y	B	Ca	Mg	REM
A1	0.016	0.010	0.011	0.15	—	—	—	—	—	—	—
A2	0.012	0.008	0.009	5.42	—	—	—	0.003	—	—	—
A3	0.008	0.006	0.012	—	3.11	2.01	0.18	—	—	—	—
A4	—	—	—	2.13	—	—	—	—	—	0.003	0.005
A5	—	—	—	—	—	—	—	—	—	—	—
A6	0.005	0.008	0.010	—	—	—	—	—	—	—	—
B1	—	—	—	5.64	—	0.89	—	0.006	—	—	—
B2	—	—	—	—	4.01	—	0.21	—	—	—	—
B3	0.008	0.008	0.009	0.98	—	—	—	—	0.005	—	—
B4	0.007	0.008	0.009	—	—	—	—	—	—	—	—
B5	0.009	0.009	0.004	1.98	—	—	—	—	—	—	—
B6	0.006	0.005	0.006	1.02	—	0.16	—	—	—	0.004	—

注) 残部は実質的にFeである。

[0086] The reheat cracking test was performed by the following approach. the welding materials which presented the restraint weld trial which extracts the welding test piece with which the long side performed 100mm to one long side from the above-mentioned base material steel plate, and the shorter side performed edge preparation with an included angle [of 30 degrees], and a root face height of 1mm by 50mm, and is shown in drawing 1 , and prepared the comparison section, a TIG-arc-welding method and MIG welding, and stick welding (SMAW) -- multilayer peak welding was performed in various combination using law. In this restraint weld trial, since other three sides except the comparison section of the welding test pieces 1 and 1 are used as a substrate 2 restraint weld 3 and are being beforehand fixed to it, thermal stress arises at the time of welding of the comparison section, and it is easy to generate a crack in that butt-welding section 4.

[0087] JIS by which the piece of a microscopic test to which the weld metal section is located in a center section after welding construction, the thickness of 5mm, width of face of 15mm, the side-bend test specimen with a die length of 100mm, and the notch were formed in the weld metal section The Charpy impact No. 4 test piece and the piece of a corrosion resistance test which are specified to Z2202 were extracted, and each following trial was presented.

[0088] After the microscopic test carried out buffing of the extracted test piece, it observed all the weld metal sections by one 400 times the scale factor of this using the optical microscope, and observed the existence of stress-relief cracking generating. Moreover, the side bend test performed 180-degree bending by board thickness twice the bend radii of 24mm of a base material, and investigated the existence of the coagulation crack in a weld metal. and the thing in which stress-relief cracking and a coagulation crack were not accepted -- success "O" and the other thing -- a rejection -- it considered as "x."

[0089] And the two above-mentioned test results performed the Charpy impact test and the corrosion resistance test only about what was success. a Charpy impact test -- 0 degree C -- carrying out -- absorbed energy -- the thing beyond 50J -- the thing below success "O" 50J -- a rejection -- it considered as "x."

[0090] the corrosion weight loss at the time of on the other hand a corrosion resistance test being immersed for 8 hours into 70% of sulfuric-acid concentration, and the sulfuric-acid water solution of 100 degrees C of solution temperature -- measuring -- the following [2.0 g/m² and hr with the corrosion rate equivalent to a base material] -- success "O" 2.0g/[m] 2 and hr super-** -- a rejection -- it considered as "x."

[0091] Table 4 and Table 5 show the analysis result of the chemical composition of the weld metal which constitutes the welded joint obtained in the above-mentioned restraint weld trial, and also show the result of each above-mentioned trial collectively. In addition, it is shown that "MIGH" in the welding process column of Table 4 is MIG welding of high dilution.

[0092]

[Table 4]

表 4

区分	試番	溶接材料	溶接方法	化 学 組 成 (質量%)														
				C	Si	Mn	P	S	Ni	Cr	Cu	Nb	Ta	Ti	Zr	Al	N	O
本 発 明 例	1	A1	TIG	0.03	0.35	1.12	0.018	0.004	52.66	18.08	1.49	1.06	0.22	—	—	0.017	0.013	0.010
	2	A2	MIG	0.05	0.40	0.87	0.016	0.003	51.38	20.48	1.21	2.32	—	0.71	—	0.014	0.011	0.009
	3	A3	TIG	0.04	0.27	0.96	0.020	0.003	41.31	17.55	1.53	0.08	—	—	0.05	0.011	0.010	0.011
	4	A4	SMAW	0.03	0.30	0.65	0.012	0.004	56.72	16.26	2.01	—	0.75	—	—	0.005	0.005	0.020
	5	A5	TIG	0.04	0.24	1.05	0.013	0.002	40.31	20.45	1.22	0.13	—	—	—	0.005	0.005	0.002
	6	A6	TIG	0.04	0.33	0.80	0.014	0.004	25.78	19.66	2.11	0.98	—	—	—	0.011	0.011	0.008
比 較 例	7	B1	MIG	0.04	0.23	1.43	0.017	0.003	36.99	18.55	2.74	—	—	—	0.06	0.004	0.004	0.002
	8	B2	TIG	0.03	*1.02	0.62	0.015	0.002	50.20	*14.04	1.39	—	—	0.18	—	0.005	0.005	0.002
	9	B3	TIG	0.02	0.31	0.96	0.016	*0.012	50.26	17.58	4.65	—	0.36	0.05	0.08	0.012	0.012	0.009
	10	B4	TIG	0.03	0.54	0.59	0.016	0.004	47.21	19.50	3.85	5.26	—	—	—	0.010	0.011	0.009
	11	B5	TIG	0.03	0.37	1.01	0.019	0.004	45.13	18.08	*8.78	1.56	—	—	0.61	0.011	0.011	0.005
	12	B6	TIG	0.04	0.30	0.87	0.014	0.003	16.64	21.29	1.36	0.77	0.08	—	—	0.009	0.009	0.007
	13	A3	MIGH	0.03	*0.35	0.96	0.020	*0.004	32.32	17.69	2.59	0.05	—	—	0.04	0.014	0.013	0.010

注1) * 印は本発明で規定する範囲を外れていることを示す。

[0093]

[Table 5]

表 5 (表4の続き)

区分	試番	化 学 組 成 (質量%)													割れ性	耐食性	E _o ℃ (J)
		Mo	W	Co	V	B	Ca	Mg	REM	①	②	③	④	⑤			
本 発 明 例	1	0.93	—	—	—	0.001	0.001	—	—	1.28	55.64	0.44	5.92	0.0049	○	○	171
	2	4.69	—	—	—	0.003	0.001	—	—	3.03	53.80	0.70	8.545	0.0075	○	○	186
	3	0.86	2.08	1.35	0.12	0.001	0.001	—	—	0.13	45.72	0.27	4.195	0.0032	○	○	183
	4	2.26	—	—	—	0.001	0.001	0.002	0.004	0.75	60.74	0.36	5.125	0.0041	○	○	169
	5	0.68	—	—	—	0.001	0.001	—	—	0.13	42.75	0.27	4.185	0.0032	○	○	170
	6	1.28	—	—	—	0.001	0.001	—	—	0.98	27.89	0.40	5.47	0.0047	○	○	181
比 較 例	7	4.97	—	0.69	—	0.005	0.001	—	—	*0.08	43.16	0.26	4.09	0.0031	×	—	—
	8	0.78	2.81	—	0.15	0.001	0.001	—	—	0.18	52.98	0.28	4.27	0.0033	×	—	—
	9	1.56	—	—	—	0.001	0.004	—	—	0.49	59.56	0.32	4.735	0.0037	×	—	—
	10	0.75	—	—	—	0.001	0.001	—	—	*5.26	54.91	1.04	11.89	0.0109	○	○	45
	11	2.14	—	—	—	0.001	0.001	—	—	2.17	62.69	0.58	7.255	0.0063	×	—	—
	12	1.48	—	0.11	—	0.001	0.001	0.003	—	0.85	*19.47	0.38	5.275	0.0043	○	×	166
	13	1.46	1.37	0.88	0.08	0.002	0.002	—	—	*0.09	38.38	0.26	4.135	0.0031	×	—	—

注1) 化学組成欄の①は式「Nb+Ta+Ti+Zr」による計算値、

②は(4)式の左辺「Ni+Co+2Cu」による計算値、

③は(1)式の右辺「0.15(Nb+Ta+Ti+Zr)+0.25」による計算値、

④は(2)式の右辺「1.5(Nb+Ta+Ti+Zr)+4.0」による計算値、

⑤は(3)式の右辺「0.0015(Nb+Ta+Ti+Zr)+0.003」による計算値である。

注2) * 印は本発明で規定する範囲を外れていることを示す。

[0094] Cracking resistance (a coagulation crack, stress-relief cracking), corrosion resistance, and the toughness of the welded joint (test numbers 1-6) of the example of this invention whose chemical composition of a weld metal is within the limits specified by this invention were good so that more clearly than Table 4 and Table 5.

[0095] On the other hand, among the welded joints (test numbers 7-13) of the example of a comparison with which the chemical entity of a weld metal separates from the range specified by this invention, since a test number 7 had few sum total contents of Nb, Ta, Ti, and Zr, the effectiveness of stress-relief cracking prevention was not acquired, but stress-relief cracking generated it. Since a test number 8 and a test number 9 had too many Si contents and S contents respectively, stress-relief cracking generated them. Although cracking resistance and corrosion resistance are good, since a test number 10 had too many sum total contents of Nb, Ta, Ti, and Zr, its toughness of a weld metal was bad.

[0096] Moreover, since a test number 12 had too few sum total contents of nickel, Co, and Cu, its corrosion resistance was bad. Although the content of Si and S itself was low, since the test number 13 had too few sum total contents of Nb, Ta, Ti, and Zr and there were too many contents of Si and S as a result, stress-relief cracking generated it.

[0097]

[Effect of the Invention] The welded joint of this invention has cracking resistance, corrosion resistance, and toughness excellent in the bottom of an extensive welding condition, does not have any problem under a high-concentration sulfuric-acid environment, and can use them.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] This invention is used for obtaining the austenitic steel welded joint excellent in the corrosion resistance which is used for elevated-temperature equipments, such as a boiler, and is especially used in a sulfuric-acid environment, and this welded joint, and relates to suitable welding materials.

[Translation done.]

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PRIOR ART

[Description of the Prior Art] Sulfur is contained in petroleum and coal which are used as fuels, such as an object for thermal power stations, and an industrial boiler. For this reason, at the time of combustion, a sulfur oxide is generated in exhaust gas. If exhaust gas temperature falls, this sulfur oxide will react with the moisture in gas, will serve as a sulfuric acid, will dew on the member front face below dew point temperature, and will produce the so-called sulfuric acid dew point corrosion.

[0003] Since the above phenomena arise, by the heat exchanger used for an exhaust gas system, the measures of holding exhaust gas temperature to an elevated temperature have been taken so that dew condensation may not arise conventionally.

[0004] However, from increase and the viewpoint of a deployment of energy need in recent years, in order to collect heat energy as effectively as possible, there is an inclination for exhaust gas temperature to become low, and in connection with this, the ingredient which has corrosion resistance to a sulfuric acid has come to be developed.

[0005] Especially, in recent years, the austenitic steel which secured corrosion resistance is proposed by adding Cu of 1 - 5 mass %, for example so that JP,4-346638,A, JP,6-128699,A, etc. may see.

[0006] When using the austenitic steel containing the above Cu(s) as the structure, it is possible to use a base material as welding materials as it is, to use the welding materials containing Cu of 2 as shown in JP,6-142980,A - 5 mass %, etc.

[0007] However, a base material receives adjustment of an organization by rolling and heat treatment after an ingot, and strong reservation is achieved. On the other hand, since a weld metal is used in the organization of a coagulation as in almost all cases, it is not easy for the segregation of an element to arise and to make corrosion resistance and reinforcement into a base material and an EQC in essence.

[0008] Therefore, when the welding materials of the same chemical composition as a base material are used, generally the corrosion resistance of a weld metal and reinforcement are inferior compared with a base material, and the welded joint equipped with the desired engine performance is hard to be obtained. Moreover, although the reinforcement in an elevated temperature was secured when the welding materials containing Cu shown in above-mentioned JP,6-142980,A were used, there was a problem that welded joints with the enough corrosion resistance in a sulfuric-acid environment were not obtained. Furthermore, the austenitic steel containing Cu shown in above-mentioned JP,4-346638,A and above-mentioned JP,6-128699,A had high weld-cracking susceptibility, and when it carried out multilayer peak welding in addition to a coagulation crack, the very very small crack occurred in the weld metal, and it had the problem that a healthy welded joint was not obtained.

[Translation done.]

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EFFECT OF THE INVENTION

[Effect of the Invention] The welded joint of this invention has cracking resistance, corrosion resistance, and toughness excellent in the bottom of an extensive welding condition, does not have any problem under a high-concentration sulfuric-acid environment, and can use them.

[Translation done.]

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The purpose of this invention is not to have a very small crack in that interior, but use for obtaining the austenitic steel welded joint excellent in the weld-cracking-proof nature which moreover shows good corrosion resistance under a sulfuric-acid environment, and a sulfuric-acid-proof corrosive, and this welded joint, and offer suitable welding materials as well as a coagulation crack, even if a weld metal is a weld metal by which multilayer peak welding was carried out.

[Translation done.]

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MEANS

[Means for Solving the Problem] The summary of this invention is in the austenitic steel welded joint excellent in the weld-cracking-proof nature of following (1), and a sulfuric-acid-proof corrosive, and the welding materials of following (2).

[0011] By mass %, (1) C:0.08% or less, less than [Mn:3%], P:0.02% or less, nickel: 4-75%, Cr:15-30%, less than [aluminum:0.5%], N:0.1% or less, In total at least one or more sorts in Nb, Ta, Ti, and Zr O (oxygen):0.1% or less 0.1 - 5%, In total both Mo, or both [either or] 0 - 20%, Co:0-5%, V:0 - 0.25%, B:0 - 0.01%, calcium:0-0.01%, Mg:0-0.01%, and REM:0-0.01% are included, and it is (1) of further the following. At Si which fills a formula, and 0 - 8% And Cu which fills the following (2) types and following (3) S which fills a formula is contained. the remainder -- substantial -- from Fe -- becoming -- (4) of the following [content / of nickel, Co, and Cu / sum total] Austenitic steel welded joint excellent in the weld-cracking-proof nature which has the weld metal section which consists of chemical composition with which a formula is filled, and a sulfuric-acid-proof corrosive.

[0012]

$Si \leq 0.15(Nb+Ta+Ti+Zr)+0.25 \text{ nickel}+Co+2Cu \geq 25$ [] (4) -- here, the symbol of element in the above-mentioned (1) - (4) type means the content (mass %) of each element in a weld metal.... (1) $Cu \leq 1.5(Nb+Ta+Ti+Zr)+4.0$ (2) $S \leq 0.0015(Nb+Ta+Ti+Zr)+0.003$.. (3)

[0013] By mass %, (2) C:0.08% or less, less than [Si:2%], less than [:Mn:3%], P:0.02% or less, S:0.02% or less, nickel:4-75%, Cr:15-30%, aluminum: Less than [0.5%], N:0.1% or less, O (oxygen):0.1% or less, In total at least one or more sorts in Nb, Ta, Ti, and Zr 0.1 - 5%, In total both Mo, or both [either or] 0 - 20%, Co:0-5%, Cu: 0-8%, V:0 - 0.25%, B:0 - 0.01%, calcium:0-0.01%, Mg:0-0.01% and REM:0-0.01% -- containing -- the remainder -- substantial -- from Fe -- becoming -- (4) of the following [content / of nickel, Co, and Cu / sum total] Welding materials which consist of chemical composition with which a formula is filled.

[0014]

$nickel+Co+2Cu \geq 25$ (4) Here, it is (4). The symbol of element in a formula means the content (mass %) of each element in welding materials.

[0015] As for the austenitic steel welded joint of this invention of the above (1), it is desirable that the base material is austenitic steel which has the chemical composition shown below. The austenitic steel is mass %. Namely, C:0.08% or less, Si: Less than [1%], less than [:Mn:2%], P:0.05% or less, S:0.01% or less, nickel: 10-30%, Cr:10-30%, Cu:2-10%, Mo:1-6%, aluminum: It is austenitic steel with which the remainder consists of Fe substantially including less than [0.5%], N:0.1% or less, O (oxygen):0.1% or less, V:0 - 0.25%, B:0 - 0.01%, calcium:0-0.01%, Mg:0-0.01%, and REM:0-0.01%.

[0016] Above-mentioned this invention was completed based on the knowledge expressed below.

[0017] When multilayer peak welding of the base material which consists of austenitic steel containing Cu is carried out using the welding materials which have the same chemical composition as a base material, it is as having mentioned above that a detailed crack occurs in a weld metal.

[0018] And it has generated in the grain boundary and the above-mentioned detailed crack is classified into the following two. That is, one of them is the stress-relief cracking of the grain boundary part into which Si and C have condensed notably, and other one is the stress-relief cracking of the grain boundary part into which S and Cu have condensed notably.

[0019] The former crack is to accept melting marks in the fracture surface, and for Si and C which were segregated to the grain boundary to combine with Fe of a matrix by the heat cycle of degree pass, to form a low melting point product, and for this to fuse. Moreover, the fracture surface is a grain boundary and the latter

crack is for the fixing force of a grain boundary to decline by the segregation of S and Cu.

[0020] As an indispensable component, the two above-mentioned kinds of crack generating can be prevented, if one or more sorts in Nb, Ta, Ti, and Zr are added.

[0021] That is, each of Nb, Ta, Ti, and Zr has a very strong affinity with C, and fixes C as a MC (M is Nb, Ta, Ti, and Zr). Moreover, these elements generate the oxide (for example, Nb (S, O)) containing S, fix S, and also make a grain boundary crystallize lamellae-like carbide during coagulation, and complicate the configuration of the grain boundary.

[0022] In order that the amount of formation of the aforementioned low melting point product may decrease sharply, it stops generating the former crack, and in order that S and Cu may carry out distributed segregation in the complicated grain boundary in addition to the oxide containing S preventing the fixing force fall of the grain boundary, it stops consequently, generating the latter crack.

[0023] However, while the above-mentioned effectiveness made one or more sorts in Nb, Ta, Ti, and Zr contain 0.1 to 5% in total, when the sum total content was made into A %, it carried out the knowledge of obtaining Si content only within the case where made Cu content below into % $(1.5 \times A + 4.0)$ below % $(0.15 \times A + 0.25)$, and S content is made below into % $(0.0015 \times A + 0.003)$.

[0024] Moreover, since it is easy to produce solidifying segregation etc. and a weld metal is used in the organization of a coagulation as as mentioned above, compared with a base material, corrosion resistance is inferior in it. However, when the sum total content (nickel+Co+2Cu) of nickel, Co, and Cu was 25% or more, the knowledge of reservation [the corrosion resistance under a high-concentration sulfuric-acid environment which the concentration of a sulfuric acid calls 70%, i.e., sulfuric-acid-proof corrosive,] being possible was carried out.

[0025]

[Embodiment of the Invention] Hereafter, the austenitic steel welded joint and welding materials of this invention are explained to a detail. In addition, "mass %" is meant "%" below.

[0026] First, the reason for having defined the chemical composition of a weld metal as mentioned above is explained.

[0027] C: 0.08% or less C is an element which makes stability the austenite phase which is a matrix. However, if it adds superfluously, while a weld thermal cycle will generate Cr carbon nitride and causing corrosion resistance degradation, it becomes the cause of a fall on the strength. Furthermore, C reacts with Fe in Si segregated to the grain boundary, and a matrix, generates a low melting point compound, and increases reheat crack sensitivity. For this reason, C content is made into 0.08% or less. A desirable upper limit is 0.05%. In addition, although the lower possible one of C content is desirable, since reduction of the degree of pole causes a cost rise, about 0.005% is sufficient as the minimum.

[0028] Si: Although added as a deoxidizer, segregate below $\{0.15 \times (\text{Nb} + \text{Ta} + \text{Ti} + \text{Zr}) + 0.25\}$ % Si to the grain boundary at the time of the coagulation of a weld metal, and it reacts with Fe of C and a matrix, generates a low melting point compound, and causes stress-relief cracking at the time of multilayer welding. If this reheat crack sensitivity adds one or more sorts in Nb, Ta, Ti, and Zr which are mentioned later and fixes C, it will fall, but if Si content exceeds $\{0.15 \times (\text{Nb} + \text{Ta} + \text{Ti} + \text{Zr}) + 0.25\}$ %, sufficient stress-relief cracking-proof nature will not be secured. For this reason, Si content is made below into $\{0.15 \times (\text{Nb} + \text{Ta} + \text{Ti} + \text{Zr}) + 0.25\}$ %. In addition, as Si content is low, when the deoxidation effectiveness needs to be acquired, it is better [when sufficient aluminum, sufficient Mn, etc. for deoxidation are included, it is not necessary to necessarily add but, and / it is good, and] to make it contain about 0.02% or more.

[0029] Mn: Mn is added as a deoxidizer 3% or less, and make stability the austenite phase which is a matrix. However, if it adds to an excess not much, while using [an elevated temperature and] long duration, generation of an intermetallic compound will be promoted, and embrittlement will be caused. For this reason, Mn content is made into 3% or less. A desirable upper limit is 2%. In addition, especially a minimum does not need to set. Moreover, when deoxidation is fully performed by other elements (Si, aluminum), additive-free is sufficient as Mn.

[0030] P: 0.02% or less P is an unescapable impurity, in the case of welding, it is segregated in the last coagulation section at the time of the coagulation of a weld metal, reduces the melting point of a residual liquid phase, and generates a coagulation crack. For this reason, P content is made into 0.02% or less. A desirable upper limit is 0.015%. In addition, as long as there is no problem in a manufacturing cost, as P content is low, it is better.

[0031] S: Below $\{0.0015x(\text{Nb}+\text{Ta}+\text{Ti}+\text{Zr})+0.003\}$ is the same unescapable impurity as the above-mentioned P, and segregate it to the grain boundary, it reduces the fixing force of a grain boundary, and causes stress-relief cracking generating while forming the eutectic object of the low melting point at the time of the coagulation of a weld metal and generating a coagulation crack in the case of welding. [S] If this reheat crack sensitivity makes the oxide which adds one or more sorts in Nb, Ta, Ti, and Zr which are mentioned later like the case of the above-mentioned Si, and contains S form and S is fixed, it will fall, but if S content exceeds $\{0.0015x(\text{Nb}+\text{Ta}+\text{Ti}+\text{Zr})+0.003\}$ %, sufficient stress-relief cracking-proof nature will not be secured. For this reason, S content is made below into $\{0.0015x(\text{Nb}+\text{Ta}+\text{Ti}+\text{Zr})+0.003\}$ %. In addition, as long as there is no problem in a manufacturing cost, as S content is low, it is better.

[0032] nickel: In order to secure the corrosion resistance in the inside of the environment containing a high-concentration sulfuric acid, 4 - 75%nickel is an indispensable element while stabilizing the austenite phase which is a matrix. In order to secure sufficient corrosion resistance, 25% or more is required of the sum total content of the amount of Co(es) and the twice as many amount of Cu(s) as this effective in raising the corrosion resistance in a sulfuric-acid environment like nickel which are mentioned later. However, while superfluous addition raises weld-cracking susceptibility, since nickel is an expensive element, it causes a cost rise. For this reason, nickel content is made into 4 - 75%.

[0033] Cr: 15-30%Cr is an effective element for reservation of oxidation-resistant [in an elevated temperature], and corrosion resistance, and in order to secure the corrosion resistance in the inside of the environment containing a high-concentration sulfuric acid, it is an indispensable element. In order to secure sufficient oxidation resistance and corrosion resistance, 15% or more is required. However, superfluous addition degrades workability remarkably while degrading corrosion resistance on the contrary. For this reason, Cr content is made into 15 - 30%. In addition, a desirable upper limit is 25%.

[0034] Form the oxide which is [in Nb, Ta, Ti, and more than Zr:1 sort] the most important element in this invention 0.1 to 5% in total, and fixes C in a weld metal as carbide, and contains S, and the fixing force of the grain boundary is raised, and also carbide is crystallized, the configuration of the grain boundary is complicated, these elements distribute the grain boundary segregation of S and Cu, and the stress-relief cracking at the time of multilayer peak welding is prevented. In order to acquire the effectiveness, it is necessary to make one or more sorts in Nb, Ta, Ti, and Zr contain 0.1% in total also at the lowest. However, the superfluous addition which exceeds 5% in total degrades workability while it causes big and rough-ization of carbide and causes degradation of toughness. For this reason, the content of these elements makes one or more sorts 0.1 - 5% in total. In addition, a desirable upper limit is 4.5.

[0035] aluminum: Although aluminum is added as a deoxidizer 0.5% or less, if contained so much, during welding, a slag will be generated, the fluidity of a weld metal and the homogeneity of a weld bead will be degraded, and welding workability will be reduced remarkably. Moreover, the welding condition field which carries out back wave formation is narrowed. For this reason, it is necessary to make aluminum content into 0.5% or less. A desirable upper limit is 0.3% and a more desirable upper limit is 0.2%.

[0036] Although N:0.1%or less N is an element effective in reservation on the strength, if contained so much, during an elevated temperature and use of long duration, it will deposit a lot of nitrides and will cause embrittlement. For this reason, N content is made into 0.1% or less. A desirable upper limit is 0.08% and a more desirable upper limit is 0.06%.

[0037] O (oxygen):0.1%or less O is an unescapable impurity, and if contained so much, cleanliness will deteriorate remarkably and it will cause embrittlement. For this reason, O content is made into 0.1% or less. A desirable upper limit is 0.08% and a more desirable upper limit is 0.06%.

[0038] Cu: Although it is less than [8%], and it is an element effective in raising the corrosion resistance in a high-concentration sulfuric-acid environment if it adds although it is not necessary to add below $\{1.5x(\text{Nb}+\text{Ta}+\text{Ti}+\text{Zr})+4.0\}$ % Cu and the effectiveness becomes remarkable at 0.5% or more, if it is made to contain exceeding 8%, the melting point of the liquid phase which carries out the last coagulation will be reduced, and a coagulation crack will be generated. Moreover, at the time of coagulation, Cu is segregated to the grain boundary, reduces the fixing force of a grain boundary, and causes the stress-relief cracking at the time of multilayer welding. As described above, since the grain boundary segregation of Cu is distributed by the complication effectiveness of the grain boundary by one or more sorts of addition of Nb, Ta, Ti, and the Zr, this reheat crack sensitivity falls, but if Cu content exceeds $\{1.5x(\text{Nb}+\text{Ta}+\text{Ti}+\text{Zr})+4.0\}$ %, sufficient stress-relief cracking-proof nature will not be secured. For this reason, Cu content in the case of adding is 8% or less, and is

good to carry out to below $\{1.5x(\text{Nb}+\text{Ta}+\text{Ti}+\text{Zr})+4.0\}$ %.

[0039] Although these elements do not need to add Mo and W:1 or more sorts 20% or less in total, if it adds, it will be an element effective in raising the corrosion resistance in a high-concentration sulfuric-acid environment, and the effectiveness will become remarkable at 1% or more of sum total contents of either or both. However, if the sum total content exceeds 20%, generation of the compound between carbide metallurgy groups will be caused [that the effectiveness is saturated and] on the contrary while in use, and it will become the cause of corrosion resistance and toughness degradation. For this reason, the content of these elements in the case of adding is good to consider as 20% or less in total.

[0040] Co: Although it is not necessary to add less than [5%] Co, if it adds, while stabilizing an austenite phase like the aforementioned nickel, it is an element effective in raising the corrosion resistance in a high-concentration sulfuric-acid environment, and the effectiveness becomes remarkable at 0.5% or more. However, Co is a very expensive element compared with the aforementioned nickel, and abundant addition causes a cost rise. For this reason, Co content in the case of adding is good to consider as 5% or less. A desirable upper limit is 4.5% and a more desirable upper limit is 4%.

[0041] Although it is not necessary to add V:0.25% or less V, if it adds, it will be an element effective in raising high temperature strength, and the effectiveness will become remarkable at 0.05% or more. However, superfluous addition deposits a lot of carbon nitride, and causes the fall of toughness. For this reason, V content in the case of adding is good to consider as 0.25% or less.

[0042] Although it is not necessary to add B:0.01% or less B, if it adds, it will segregate to the grain boundary and the reinforcement of a grain boundary will be raised, it is the element which has the effectiveness of reducing reheat crack sensitivity, and the effectiveness becomes remarkable at 0.0005% or more. However, superfluous addition promotes the coagulation crack at the time of welding conversely. For this reason, B content in the case of adding is good to consider as 0.01% or less. A desirable upper limit is 0.009% and a more desirable upper limit is 0.008%.

[0043] calcium: Although it is not necessary to add calcium 0.01% or less, if it adds, an affinity with S is strong, a sulfide will be formed, S will be fixed, it will be the element which has the effectiveness which raises stress-relief cracking-proof nature, and the effectiveness will become remarkable at 0.0005% or more. However, superfluous addition makes inclusion increase and degrades cleanliness. For this reason, calcium content in the case of adding is good to consider as 0.01% or less. A desirable upper limit is 0.009% and a more desirable upper limit is 0.008%.

[0044] Mg: Although it is not necessary to add Mg 0.01% or less, if it adds, like the above-mentioned calcium, an affinity with S is strong, a sulfide will be formed, S will be fixed, it will be the element which has the effectiveness which raises stress-relief cracking-proof nature, and the effectiveness will become remarkable at 0.0005% or more. However, superfluous addition makes inclusion increase and degrades cleanliness. For this reason, Mg content in the case of adding is good to consider as 0.01% or less. A desirable upper limit is 0.009% and a more desirable upper limit is 0.008%.

[0045] REM: Although it is not necessary to add REM 0.01% or less, if it adds, an affinity with S is strong, the amount of S which generates a high-melting sulfide and is segregated to the grain boundary will be reduced, it will be the element which has the effectiveness of reducing reheat crack sensitivity, and the effectiveness will become remarkable at 0.0005% or more. However, it causes a toughness fall while superfluous addition makes inclusion increase, spoils cleanliness and degrades corrosion resistance on the contrary. For this reason, the REM content in the case of adding is good to consider as 0.01% or less. A desirable upper limit is 0.009% and a more desirable upper limit is 0.008%.

[0046] It is desirable to use the austenitic steel which has the following chemical composition for the austenitic steel of the base material which constitutes the austenitic steel welded joint of this invention equipped with the weld metal which has the above-mentioned chemical composition.

[0047] The austenitic steel is mass %. Namely, C:0.08% or less, Si: Less than [1%], less than [:Mn:2%], P:0.05% or less, S:0.01% or less, nickel: 10-30%, Cr:10-30%, Cu:2-10%, Mo:1-6%, aluminum: It is austenitic steel with which the remainder consists of Fe substantially including less than [0.5%], N:0.1% or less, O:0.1% or less, B:0 - 0.01%, calcium:0-0.01%, Mg:0-0.01%, and REM:0-0.01%, and the reason is as follows.

[0048] Since Cr carbon nitride generates C especially in a heat affected zone and it becomes impossible to secure desired corrosion resistance when the content exceeds 0.08%, it is desirable. [0.08% or less of]

[0049] Since Si content in a weld metal will increase and the reheat crack sensitivity of a weld metal will

become high by dilution if the content exceeds 1%, 1% or less of Si is desirable.

[0050] Although Mn is added as a deoxidizer, if superfluous addition is carried out extremely, since an intermetallic compound will be generated while using an elevated temperature and embrittlement will be caused, 2% or less is desirable.

[0051] Since P content of P in a weld metal will increase and coagulation crack sensitivity will raise it by dilution if the content exceeds 0.05%, 0.05% or less is desirable.

[0052] Since S content in a weld metal will increase and the reheat crack sensitivity of a weld metal will become high by dilution if the content exceeds 0.01%, 0.01% or less of S is desirable.

[0053] Since nickel will cause increase of a manufacturing cost if an austenite phase becomes it unstable that the content is less than 10% and it exceeds 30% conversely, 10 - 30% is desirable.

[0054] Since Cr will cause a deposit of a lot of carbide and will reduce toughness while workability deteriorates remarkably, and using [a heat affected zone or] an elevated temperature if corrosion resistance becomes it inadequate that the content is less than 10% and it exceeds 30% conversely, it is desirable. [10 - 30% of]

[0055] Since workability will deteriorate remarkably if the corrosion resistance under a high-concentration sulfuric-acid environment becomes non-** for the content to be less than 2% and it exceeds 10% conversely, 2 - 10% of Cu is desirable.

[0056] Since Mo will cause generation of a lot of compounds between carbide metallurgy groups and will reduce toughness while using [a weld thermal cycle or] an elevated temperature if the corrosion resistance under a high-concentration sulfuric-acid environment becomes non-** for the content to be less than 1% and it exceeds 6% conversely, it is desirable. [1 - 6% of]

[0057] As for aluminum, N, and O (oxygen), it is desirable that each is [aluminum] 0.1% or less about 0.5% or less, and N and O by the same reason as the case of a weld metal.

[0058] Although B does not need to contain, since the content of B content in a weld metal increases depending on super-***** and dilution 0.01% and the coagulation crack sensitivity of a weld metal becomes high when it contains, as for B content in the case of containing, it is desirable that it is 0.01% or less.

[0059] Although all calcium, Mg, and REM need to contain, when it contains, as for the content of these elements since 0.01% super-*****, and inclusion increase and spoil cleanliness, in case the content contains any element, it is desirable that any element is 0.01% or less.

[0060] In addition, B, calcium, Mg, and REM in the case of containing raise hot-working nature. Moreover, about REM, when it dilutes in a weld metal, a high-melting sulfide is formed, S segregation to the grain boundary is controlled, and the stress-relief cracking nature susceptibility of a weld metal is reduced.

[0061] Moreover, it uses in order to obtain the weld metal which has the above-mentioned chemical composition which constitutes the austenitic steel welded joint of this invention, and suitable welding materials are welding materials which have the following chemical composition.

[0062] The welding materials are mass %. Namely, C:0.08% or less, less than [Si:2%], : Less than [Mn:3%], P:0.02% or less, S:0.02% or less, nickel:4-75%, Cr: 15-30%, less than [aluminum:0.5%], N:0.1% or less, O:0.1% or less, In total at least one or more sorts in Nb, Ta, Ti, and Zr 0.1 - 5%, In total both Mo, or both [either or] 0 - 20%, Co:0-5%, Cu: 0-8%, V:0 - 0.25%, B:0 - 0.01%, calcium:0-0.01%, Mg: It is ***** which the remainder consists of Fe substantially and consists of chemical composition with which the sum total content of nickel, Co, and Cu fills a formula "nickel+Co+2Cu>=25" including 0-0.01% and REM:0-0.01%, and the reason is as follows.

[0063] In order to give sufficient engine performance for a weld metal, as for C content, it is desirable that it is 0.08% or less.

[0064] Since Si will increase Si content in a weld metal and will increase reheat crack sensitivity while it degrades remarkably the hot-working nature at the time of welding-materials manufacture if the content exceeds 2%, it is desirable that it is 2% or less.

[0065] Since Mn will cause generating of a lot of fume at the time of welding while degrading the hot-working nature at the time of welding-materials manufacture if the content exceeds 3%, it is desirable that it is 3% or less.

[0066] As for P content, it is desirable that it is 0.02% or less by the same reason as the case of a weld metal.

[0067] Since S will increase S content in a weld metal and will increase coagulation crack sensitivity and reheat crack sensitivity while it degrades the hot-working nature at the time of welding-materials manufacture if the content exceeds 0.02%, it is desirable that it is 2% or less.

[0068] As for nickel content, it is desirable that it is the amount which is 4 - 75% and fills a formula "nickel+Co+2Cu>=25" for the same reason as the case of a weld metal.

[0069] In order to give sufficient stress-relief cracking-proof nature for a weld metal, as for Cr content, it is desirable that it is 10 - 30%.

[0070] Although Nb, Ta, Ti, and Zr make one or more sorts contain as an indispensable component, in order to give sufficient stress-relief cracking-proof nature for a weld metal, as for the content, it is desirable that it is 0.1 - 5% in total.

[0071] As for each content of aluminum, N, and O (oxygen), it is desirable that each is [aluminum] 0.1% or less about 0.5% or less, and N and O by the same reason as the case of a weld metal.

[0072] Although Cu does not need to contain, since the content reduces remarkably the hot-working nature at the time of 8% super-*****, and welding-materials manufacture when it contains, as for the content in the case of containing, it is desirable that it is 8% or less.

[0073] Although Mo and W do not need to contain, in order to give the engine performance required for a weld metal, as for a content in case either or both are included, it is desirable that it is 20% or less in total.

[0074] Although Co does not need to contain, in order to give the engine performance required for a weld metal, as for the content in the case of containing, it is desirable that it is 5% or less.

[0075] Although V may not have *****, in order to give the engine performance required for a weld metal, as for the content in the case of containing, it is desirable that it is 0.25% or less.

[0076] Although B does not need to contain, in order to give the engine performance required for a weld metal, as for the content in the case of containing, it is desirable that it is 0.01% or less.

[0077] Although all calcium, Mg, and REM need to contain, in order to give the engine performance required for a weld metal, as for the content of each element in the case of containing, it is desirable that any element is 0.01% or less.

[0078] In addition, B, calcium, above-mentioned Mg, and above-mentioned REM in the case of containing raise hot-working nature. Moreover, about REM, a high-melting sulfide is formed, S segregation to the grain boundary is controlled, and the reheat crack sensitivity of a weld metal is reduced.

[0079] what has the chemical composition the weld metal prescribes the above-mentioned welded joint which becomes this invention by this invention -- it is even -- if it carries out -- TIG -- law and MIG -- even when there is no effect by welding processes, such as a gas-shielded-arc-welding method represented by law, a stick welding method, and a submerged-arc-welding method, and it manufactures with which welding process, sufficient weld-cracking-proof nature and a sulfuric-acid-proof corrosive are shown.

[0080] Moreover, there are no special conditions in the welding condition in the case of manufacturing the above-mentioned welded joint which becomes this invention with each above-mentioned welding process.

[Translation done.]

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EXAMPLE

[Example] The base material steel plate of 12mm of board thickness which has the chemical composition shown in Table 1 was prepared. The corrosion rates per unit area when this base material steel plate is immersed for 8 hours into the sulfuric-acid solution which is 100 degrees C of solution temperature whose sulfuric-acid concentration is 70% are below 2.0 g/m² and hr.

[0082]

[Table 1]

表 1

化 学 組 成 (質量%)							
C	Si	Mn	P	S	Ni	Cu	Cr
0.02	0.50	0.96	0.020	0.005	15.12	4.62	17.96

Mo	Al	N	O	B	Ca
2.60	0.018	0.018	0.008	0.003	0.003

注) 残部は実質的にFeである。

[0083] Moreover, it has the chemical composition shown in Table 2 and Table 3, and the welding materials (welding wire) which are 12 kinds whose outer diameters are 1.2mm were prepared except No.A4. In addition, the welding materials of No.A4 are the covered electrodes which applied the cladding material which becomes the periphery of a welding wire with an outer diameter of 4mm from a metal carbonate, metal fluoride, Si compound, Ti compound, and metal powder.

[0084]

[Table 2]

表 2

No	化 学 組 成 (質量%)											
	C	Si	Mn	P	S	Ni	Cr	Cu	Nb	Ta	Ti	Zr
A1	0.04	0.28	1.20	0.017	0.004	70.32	18.13	0.01	1.56	0.33	—	—
A2	0.06	0.36	0.84	0.015	0.002	64.12	21.36	0.01	3.13	—	0.96	—
A3	0.05	0.15	0.96	0.020	0.002	54.21	17.35	0.01	0.12	—	—	0.08
A4	0.03	0.23	0.54	0.009	0.004	72.11	15.63	1.05	—	1.03	—	—
A5	0.05	0.15	1.08	0.011	0.001	49.16	21.33	0.03	0.18	—	—	—
A6	0.06	0.20	0.75	0.010	0.003	31.18	20.18	—	2.02	—	—	—
B1	0.04	0.16	1.56	0.016	0.003	43.16	18.71	2.21	—	—	—	0.08
B2	0.04	1.24	0.48	0.013	0.001	85.23	12.36	0.01	—	—	0.26	—
B3	0.02	0.21	0.96	0.014	0.016	70.02	17.36	4.67	—	0.56	0.08	0.12
B4	0.03	0.56	0.44	0.015	0.003	60.32	20.13	3.54	7.41	—	—	—
B5	0.03	0.33	1.03	0.018	0.003	55.13	18.12	10.16	2.08	—	—	0.81
B6	0.05	0.22	0.84	0.011	0.002	17.26	22.65	0.03	1.08	0.11	—	—

[0085]

[Table 3]

表 3 (表2の続き)

No.	化 学 組 成 (質量%)										
	Al	N	O	Mo	W	Co	V	B	Ca	Mg	REM
A1	0.016	0.010	0.011	0.15	—	—	—	—	—	—	—
A2	0.012	0.008	0.009	5.42	—	—	—	0.003	—	—	—
A3	0.008	0.006	0.012	—	3.11	2.01	0.18	—	—	—	—
A4	—	—	—	2.13	—	—	—	—	—	0.003	0.005
A5	—	—	—	—	—	—	—	—	—	—	—
A6	0.005	0.008	0.010	—	—	—	—	—	—	—	—
B1	—	—	—	5.64	—	0.89	—	0.008	—	—	—
B2	—	—	—	—	4.01	—	0.21	—	—	—	—
B3	0.008	0.008	0.009	0.88	—	—	—	—	0.005	—	—
B4	0.007	0.008	0.009	—	—	—	—	—	—	—	—
B5	0.009	0.009	0.004	1.98	—	—	—	—	—	—	—
B6	0.006	0.005	0.006	1.02	—	0.16	—	—	—	0.004	—

注) 残部は実質的にFeである。

[0086] The reheat cracking test was performed by the following approach. the welding materials which presented the restraint weld trial which extracts the welding test piece with which the long side performed 100mm to one long side from the above-mentioned base material steel plate, and the shorter side performed edge preparation with an included angle [of 30 degrees], and a root face height of 1mm by 50mm, and is shown in drawing 1 , and prepared the comparison section, a TIG-arc-welding method and MIG welding, and stick welding (SMAW) -- multilayer peak welding was performed in various combination using law. In this restraint weld trial, since other three sides except the comparison section of the welding test pieces 1 and 1 are used as a substrate 2 restraint weld 3 and are being beforehand fixed to it, thermal stress arises at the time of welding of the comparison section, and it is easy to generate a crack in that butt-welding section 4.

[0087] JIS by which the piece of a microscopic test to which the weld metal section is located in a center section after welding construction, the thickness of 5mm, width of face of 15mm, the side-bend test specimen with a die length of 100mm, and the notch were formed in the weld metal section The Charpy impact No. 4 test piece and the piece of a corrosion resistance test which are specified to Z2202 were extracted, and each following trial was presented.

[0088] After the microscopic test carried out buffing of the extracted test piece, it observed all the weld metal sections by one 400 times the scale factor of this using the optical microscope, and observed the existence of stress-relief cracking generating. Moreover, the side bend test performed 180-degree bending by board thickness twice the bend radii of 24mm of a base material, and investigated the existence of the coagulation crack in a weld metal. and the thing in which stress-relief cracking and a coagulation crack were not accepted -- success "O" and the other thing -- a rejection -- it considered as "x."

[0089] And the two above-mentioned test results performed the Charpy impact test and the corrosion resistance test only about what was success. a Charpy impact test -- 0 degree C -- carrying out -- absorbed energy -- the thing beyond 50J -- the thing below success "O" 50J -- a rejection -- it considered as "x."

[0090] the corrosion weight loss at the time of on the other hand a corrosion resistance test being immersed for 8 hours into 70% of sulfuric-acid concentration, and the sulfuric-acid water solution of 100 degrees C of solution temperature -- measuring -- the following [2.0 g/m2 and hr with the corrosion rate equivalent to a base material] -- success "O" 2.0g/[m] 2 and hr super-** -- a rejection -- it considered as "x."

[0091] Table 4 and Table 5 show the analysis result of the chemical composition of the weld metal which constitutes the welded joint obtained in the above-mentioned restraint weld trial, and also show the result of each above-mentioned trial collectively. In addition, it is shown that "MIG" in the welding process column of Table 4 is MIG welding of high dilution.

[0092]

[Table 4]

表 4

区分	試番	溶接材料	溶接方法	化 学 組 成 (質量%)														
				C	Si	Mn	P	S	Ni	Cr	Cu	Nb	Ta	Ti	Zr	Al	N	O
本 発 明 例	1	A1	TIG	0.03	0.35	1.12	0.018	0.004	52.66	18.08	1.49	1.06	0.22	—	—	0.017	0.013	0.010
	2	A2	MIG	0.05	0.40	0.87	0.016	0.003	51.38	20.48	1.21	2.32	—	0.71	—	0.014	0.011	0.009
	3	A3	TIG	0.04	0.27	0.96	0.020	0.003	41.31	17.55	1.53	0.08	—	—	0.05	0.011	0.010	0.011
	4	A4	SMAW	0.03	0.30	0.65	0.012	0.004	56.72	16.26	2.01	—	0.75	—	—	0.005	0.005	0.020
	5	A5	TIG	0.04	0.24	1.05	0.013	0.002	40.31	20.45	1.22	0.13	—	—	—	0.005	0.005	0.002
	6	A6	TIG	0.04	0.33	0.80	0.014	0.004	25.78	19.66	2.11	0.98	—	—	—	0.011	0.011	0.008
比 較 例	7	B1	MIG	0.04	0.23	1.43	0.017	0.003	36.99	18.55	2.74	—	—	—	0.06	0.004	0.004	0.002
	8	B2	TIG	0.03	*1.02	0.62	0.015	0.002	50.20	*14.04	1.39	—	—	0.18	—	0.005	0.005	0.002
	9	B3	TIG	0.02	0.31	0.96	0.016	*0.012	50.26	17.58	4.65	—	0.36	0.05	0.08	0.012	0.012	0.009
	10	B4	TIG	0.03	0.54	0.59	0.016	0.004	47.21	19.50	3.85	5.26	—	—	—	0.010	0.011	0.009
	11	B5	TIG	0.03	0.37	1.01	0.019	0.004	45.13	18.08	*8.78	1.56	—	—	0.61	0.011	0.011	0.005
	12	B6	TIG	0.04	0.30	0.87	0.014	0.003	16.64	21.29	1.36	0.77	0.08	—	—	0.009	0.009	0.007
	13	A3	MIG	0.03	*0.35	0.96	0.020	*0.004	32.32	17.69	2.59	0.05	—	—	0.04	0.014	0.013	0.010

注1) * 印は本発明で規定する範囲を外れていることを示す。

[0093]

[Table 5]

表 5 (表4の続き)

区分	試番	化 学 組 成 (質量%)													割れ性	耐食性	E _o ℃ (J)
		Mo	W	Co	V	B	Ca	Mg	REM	①	②	③	④	⑤			
本 発 明 例	1	0.93	—	—	—	0.001	0.001	—	—	1.28	55.64	0.44	5.92	0.0049	○	○	171
	2	4.69	—	—	—	0.003	0.001	—	—	3.03	53.80	0.70	8.545	0.0075	○	○	186
	3	0.86	2.08	1.35	0.12	0.001	0.001	—	—	0.13	45.72	0.27	4.195	0.0032	○	○	183
	4	2.26	—	—	—	0.001	0.001	0.002	0.004	0.75	60.74	0.36	5.125	0.0041	○	○	169
	5	0.68	—	—	—	0.001	0.001	—	—	0.13	42.75	0.27	4.195	0.0032	○	○	170
	6	1.28	—	—	—	0.001	0.001	—	—	0.98	27.89	0.40	5.47	0.0047	○	○	181
比 較 例	7	4.97	—	0.69	—	0.005	0.001	—	—	*0.06	43.16	0.26	4.09	0.0031	×	—	—
	8	0.78	2.81	—	0.15	0.001	0.001	—	—	0.18	52.98	0.28	4.27	0.0033	×	—	—
	9	1.56	—	—	—	0.001	0.004	—	—	0.49	59.56	0.32	4.735	0.0037	×	—	—
	10	0.75	—	—	—	0.001	0.001	—	—	*5.26	54.91	1.04	11.89	0.0109	○	○	45
	11	2.14	—	—	—	0.001	0.001	—	—	2.17	62.69	0.58	7.255	0.0063	×	—	—
	12	1.48	—	0.11	—	0.001	0.001	0.003	—	0.85	*19.47	0.38	5.275	0.0043	○	×	166
	13	1.46	1.37	0.88	0.08	0.002	0.002	—	—	*0.09	38.38	0.26	4.135	0.0031	×	—	—

注1) 化学組成欄の①は式「Nb+Ta+Ti+Zr」による計算値、

②は(4) 式の左辺「Ni+Co+2Cu」による計算値、

③は(1) 式の右辺「0.15(Nb+Ta+Ti+Zr)+0.25」による計算値、

④は(2) 式の右辺「1.5(Nb+Ta+Ti+Zr)+4.0」による計算値、

⑤は(3) 式の右辺「0.0015(Nb+Ta+Ti+Zr)+0.003」による計算値である。

注2) * 印は本発明で規定する範囲を外れていることを示す。

[0094] Cracking resistance (a coagulation crack, stress-relief cracking), corrosion resistance, and the toughness of the welded joint (test numbers 1-6) of the example of this invention whose chemical composition of a weld metal is within the limits specified by this invention were good so that more clearly than Table 4 and Table 5.

[0095] On the other hand, among the welded joints (test numbers 7-13) of the example of a comparison with which the chemical entity of a weld metal separates from the range specified by this invention, since a test number 7 had few sum total contents of Nb, Ta, Ti, and Zr, the effectiveness of stress-relief cracking prevention was not acquired, but stress-relief cracking generated it. Since a test number 8 and a test number 9 had too many Si contents and S contents respectively, stress-relief cracking generated them. Although cracking resistance and corrosion resistance are good, since a test number 10 had too many sum total contents of Nb, Ta, Ti, and Zr, its toughness of a weld metal was bad.

[0096] Moreover, since a test number 12 had too few sum total contents of nickel, Co, and Cu, its corrosion resistance was bad. Although the content of Si and S itself was low, since the test number 13 had too few sum total contents of Nb, Ta, Ti, and Zr and there were too many contents of Si and S as a result, stress-relief cracking generated it.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing showing the test method of a reheat cracking test, and this drawing (a) is a top view and this drawing (b) is a cross-sectional view.

[Description of Notations]

- 1: Welding test piece,
- 2: Substrate,
- 3: Restraint weld,
- 4: Butt-welding section.

[Translation done.]

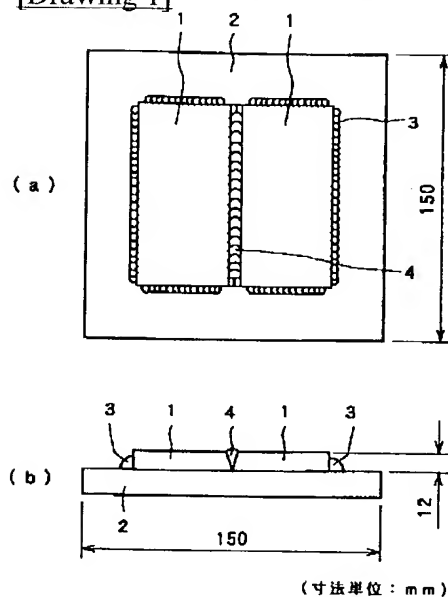
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DRAWINGS

[Drawing 1]



[Translation done.]